Complete separability of the Stark problem in hydrogen

1979 J. Phys. A: Math. Gen. 12 L193

(http://iopscience.iop.org/0305-4470/12/7/009)

J. Phys. A: Math. Gen., Vol. 12, No. 7, 1979. Printed in Great Britain

LETTER TO THE EDITOR

Complete separability of the Stark problem in hydrogen

S Graffi†, V Grecchi‡ and B Simon§

† Istituto Matematico, Università di Modena, Italy
‡ Istituto Matematico and Istituto di Fisica, Università di Modena, Italy
§ Department of Mathematics and Physics, Princeton University, Princeton NJ, USA
Research partially supported by U.S.N.S.F Grant MCS-78-01885.

Received 20 March 1979

Abstract. We prove that every fixed m resonance eigenfunction of hydrogen in a constant electric field is a *finite* sum of functions which are products in squared parabolic coordinates. This shows that the standard *ansatz* yields all resonances.

This note represents a contribution to the rapidly developing rigorous theory of resonances of atoms, especially hydrogen, in constant electric fields (Benassi *et al* 1979; Benassi and Grecchi, in preparation; Graffi and Grecchi 1978, 1979; Harrell and Simon in preparation; Herbst 1979; Herbst and Simon 1978, in preparation).

Separability of the classical problem of a charged particle in a Coulomb plus constant field in elliptic coordinates was noted by Jacobi (1884). In an attempt to analyse Stark's experimental results within the Bohr–Sommerfeld theory, Epstein (1916) introduced squared parabolic coordinates which were then exploited in the 'new' quantum theory independently by Epstein (1926) and Schrödinger (1926). To explain the problem we shall solve here, let us begin with a formal description of the separation. Let (ρ, z, ϕ) be the usual cylindrical coordinates and let

$$r=(\rho^2+z^2)^{1/2}, \qquad u=(r+z)^{1/2}, \qquad v=(r-z)^{1/2}; \tag{1}$$

(u and v are called 'squared parabolic coordinates' since u^2 and v^2 are the usual parabolic coordinates). For later purposes, we note the Jacobian relation

$$(uv)\,\mathrm{d}u\,\mathrm{d}v=\tfrac{1}{2}r^{-1}(\rho\,\mathrm{d}\rho\,\mathrm{d}z), \tag{2}$$

which is easy to check. The Epstein–Schrödinger *ansatz* notes that if

$$\mu(\boldsymbol{r})=(uv)^{-1/2}\psi(u)\omega(v)\exp(\mathrm{i}m\phi) \tag{3}$$

with

$$(-\mathrm{d}^2/\mathrm{d}u^2-Eu^2+\tfrac{1}{2}Fu^4+(m^2-\tfrac{1}{4})u^{-2})\psi=\Lambda_1\psi, \tag{4a}$$

$$(-\mathrm{d}^2/\mathrm{d}v^2-Ev^2-\tfrac{1}{2}Fv^4+(m^2-\tfrac{1}{4})v^{-2})\omega=\Lambda_2\omega, \tag{4b}$$

and

$$\Lambda_1+\Lambda_2=2Z, \tag{5}$$

then

$$(-\Delta-Zr^{-1}-Fz)\mu=E\mu. \tag{6}$$

Our goal in this Letter is to show that every 'resonance solution' of (6) is indeed of the form (3, 4, 5) (or more precisely a *finite* sum thereof) so that no resonances are lost by presupposing the *ansatz* (3). This answers a question raised by J Fröhlich (private communication).

We answer the question within the complex scaling formalism of resonances due to Balslev and Combes (1971), extended to the Stark problem by two of us (Graffi and Grecchi 1971) for resonances obeying the Epstein–Schrödinger *ansatz*, and independently by Herbst in the general case (see also Herbst and Simon 1978 and in preparation). Among the consequences of our result are the following: (*a*) It fills a gap in Graffi and Grecchi 1979, namely certain results claimed there for *all* resonances were only proven for those given by an analogue of the implicit equation (5); here we show that every resonance is of this form; (*b*) It justifies the work of many others who have studied the Stark problem in hydrogen with the unspoken assumption that all resonances obey the *ansatz* (3); (*c*) From the known fall off of solutions of (4) as $u, v \to \exp(\mathrm{i}\theta)u, \exp(\mathrm{i}\theta)v$ ($\mathrm{Im}\ \theta \neq 0$ and small) one can read off the exponential fall off of $\mu(\rho, z, \phi)$ after the change $\rho, z \to \exp(2\mathrm{i}\theta)u, \exp(2\mathrm{i}\theta)v$ (as $\exp[-(|r|^{3/2})]$. This has already been proven by Herbst and Simon (in preparation) by other means for general atoms.

We should explain why the problem at hand is harder than the more usual separability problems in quantum mechanics. In the first place, the role of E is changed: after the change of variables, it is no longer an eigenvalue and is rather given by the implicit equation (5).

More serious is the following: in the usual problems, one is dealing with self-adjoint operators, and the justification of complete separability is a consequence of the spectral theorem. After the complex scaling, one is dealing with non-self-adjoint operators and the spectral theorem is no longer available.

We shall therefore have to use more sophisticated tools, namely various ideas on the spectrum of tensor products (Brown and Pearcy 1966; Schechter 1969; Ichinose 1970; Reed and Simon 1978) originating in Brown and Pearcy (1966) and theorems of Keldys (1951) that guarantee the completeness of the generalised eigenvectors of certain operators (see also Reed and Simon (1978)).

To be explicit, let F, Z be real, $F > 0$, and define for $0 < \mathrm{Im}\ \theta < \pi/3$:

$$H(F, Z, \theta) = -\exp(-2\theta)\Delta - \exp(-\theta)Zr^{-1} + \exp(\theta)Fz \tag{7}$$

and let

$$h_m(\alpha, \beta) = \mathrm{d}^2/\mathrm{d}x^2 + \alpha x^2 + \beta x^4 + (m^2 - \tfrac{1}{4})x^{-2} \tag{8}$$

with $\beta \notin [-\infty, 0]$ and α both complex. h_m has a discrete spectrum (see e.g. Graffi and Grecchi 1978) as does $H(F, Z, \theta)$ (Herbst 1979). By definition, resonance energies are eigenvalues of (7); they are independent of θ in the region. Since H leaves the set of functions with $L_z = m$ invariant, one need only consider the operator H restricted to a fixed $L_z = m$ subspace; call it H_m. Our main result is the following:

Theorem 1. Fix $F > 0$, Z real and θ with $0 < \mathrm{Im}\ \theta < \pi/3$. Let μ be a function with

$$H_m(F, Z, \theta)\mu = E\mu;$$

then μ is a finite sum of functions of the form

$$\mu_\alpha(\boldsymbol{r}) = (uv)^{-1/2}\psi(u)\omega(v)\exp(\mathrm{i}m\phi) \tag{3'}$$

with

$$\exp(\mathrm{i}-\mathrm{i}\theta)h_m(-\exp(2\mathrm{i}\theta)E, \tfrac{1}{2}\exp(3\mathrm{i}\theta)F)\psi = \Lambda_1\psi, \tag{4a'}$$

$$\exp(-\mathrm{i}\theta)h_m(-\exp(2\mathrm{i}\theta)E, \tfrac{1}{2}\exp(3\mathrm{i}\theta - \mathrm{i}\pi)F)\omega = \Lambda_2\omega \tag{4b'}$$

$$\Lambda_1 + \Lambda_2 = 2Z \tag{5}$$

In particular, if $\mu_k^{(m)}(\alpha, \beta)$ are the eigenvalues of $h_m(\alpha, \beta)$, then E obeys the implicit equation

$$\mu_k^{(m)}(-\exp(2\mathrm{i}\theta)E, \tfrac{1}{2}\exp(3\mathrm{i}\theta)F) + \mu_{k_2}^{(m)}(-\exp(2\mathrm{i}\theta)E, \tfrac{1}{2}\exp(3\mathrm{i}\theta - \mathrm{i}\pi)F) = 2\exp(\mathrm{i}\theta)Z. \tag{9}$$

Remarks: 1. It is only for notational convenience that we take F real; one can allow complex F as in Graffi and Grecchi (1978); Herbst (1979); Herbst and Simon (1978, in preparation).

2. While we deal only with resonances, i.e. solutions of $(H-E)\mu = 0$, it is possible that there are Jordan anomalies, i.e. E, μ with $(H-E)^k\mu = 0$, $(H-E)^{k-1}\mu \neq 0$.

Our proof below then shows that they are given by finite sums of the form (3′) with now $(\exp(-\mathrm{i}\theta)h_m(\cdot) - \Lambda_1)^l\psi = 0$ for some $l \leq k$, etc.

The proof of our theorem is in several steps:

Proof: Step 1. Let

$$\psi(u, v) = (uv)^{1/2}\mu(r)\exp(-\mathrm{i}m\phi). \tag{10}$$

Then we claim that

$$I = \int^{\infty}\int^{\infty} |\Psi(u, v)|^2\, \mathrm{d}u\, \mathrm{d}v < \infty. \tag{11}$$

For by the change of variables formula (2), the integral equals (we use $\int \mathrm{d}\phi = 2\pi$)

$$I = \frac{1}{4\pi}\int |\mu(r)|^2 r^{-1}\, \mathrm{d}^3r$$

so that (11) follows from the fact that (Herbst 1979)

$$D(H(F, Z, \tau)) = D(-\Delta) \cap D(z),$$

and the standard operator inequality (hydrogen is bounded below!)

$$r^{-1} \leq c(-\Delta + I).$$

Step 2. Let

$$A = \exp(-\mathrm{i}\theta)h_m(-\exp(2\mathrm{i}\theta)E, \tfrac{1}{2}\exp(3\mathrm{i}\theta)F),$$

$$B = \exp(-\mathrm{i}\theta)h_m(-\exp(2\mathrm{i}\theta)E, \tfrac{1}{2}\exp(3\mathrm{i}\theta - \mathrm{i}\pi)F),$$

$$C = A \otimes I + I \otimes B, \tag{12}$$

on $L^2(\mathrm{d}u\, \mathrm{d}v)$. Then we claim that

$$C\Psi = 2Z\Psi. \tag{13}$$

This is merely the formal change of variables which easily establishes (12) in the distributional sense from which (12) follows.

Step 3. Recall that an operator D is called strictly m-accretive if and only if there exists $\varepsilon > 0$ such that for all ϕ in its domain

$$|\arg(\phi, D\phi)| < \pi/2 - \epsilon. \tag{14}$$

Then we claim that $\exp(-i\theta/2)(A + c_1)$ and $\exp(i\theta/2)\exp(i\pi/6)(B + c_2)$ are strictly m-accretive for suitable constants c_1 and c_2. If one drops the quadratic term this is trivially true with $c_1 = 0$ (take $\epsilon = (3/2)(\pi/3 - \theta)$ for A and $\epsilon = 3\theta/2$ for B). The constant term and the inequality $(\phi, x^2\phi) \leq (\phi, x^4\phi)^{1/2}(\phi, \phi)$ can then take care of the quadratic term. Moreover by the same reasoning both $\exp(i\alpha)(A + \tilde{C}_1) = \tilde{A}$ and $\exp(i\alpha)(B + \tilde{C}_2) = \tilde{B}$ with $\alpha = \pi/2 - 2i\theta$ (same α) are m-accretive (i.e. (14) holds with $\epsilon = 0$).

Thus $P = \exp(-\tilde{A})$ and $Q = \exp(-\tilde{B})$ are bounded operators and ψ is an eigenfunction of $P \otimes Q$. (Unfortunately P and Q are not compact.)

Step 4. Now we claim that A and B have trace-class resolvents. For by an elementary estimate (Simon 1970) $(A + c)^{-1}(p^2 + x^4)$ and $(B + c)^{-1}(p^2 + x^4)$ are bounded so this follows from the fact that $(p^2 + x^4 + 1)^{-1}$ is trace-class since its nth eigenvalue goes as $n^{-4/3}$ by a WKB type estimate.

Step 5. P and Q are bounded operators with a complete set of generalised eigenvectors. (ψ is a generalised eigenvector of D if $(D - E)^k\psi = 0$ for some k). This follows from a result of Keldys (1951) (see Theorem XIII, 101 and its Corollary in Reed and Simon (1978)) given steps 3 and 4. Completeness means, let us recall, that finite linear combinations are dense.

Step 6. We next claim that the eigenvalues λ_n of P go to zero as $n \to \infty$ and similarly for Q. Thus if μ_n are the eigenvalues of $\tilde{A}$ ordered by increasing $|\mu_n|$, we claim that as $n \to \infty |\arg \mu_n|$ stays strictly away from $\pm\pi/2$. Since $\tilde{A}$ has a numerical range near the imaginary axis, this is somewhat subtle. The point is that

$$\tilde{A} = \tilde{\alpha}p^2 + \tilde{\beta}x^2 + \tilde{\gamma}x^4$$

with $|\alpha|, |\gamma| \neq 0$ and both arguments inside a sector of opening angle less than $\pi/2$. By a scaling $\alpha \to \alpha \exp(2i\psi)$, $\gamma \to \gamma \exp(-4i\psi)$, $\beta \to \beta \exp(-2i\psi)$ which leaves the eigenvalue spectrum invariant (Simon 1970) we can arrange that $\tilde{A}$ is taken into an operator $\hat{A}$ of the same form with $\arg\hat{\alpha} = \arg\hat{\gamma} = \frac{1}{3}(2\arg\hat{\alpha} + \arg\tilde{\gamma})$ which is away from $\pm\pi/2$. We claim that this angle is the asymptotic phase of the eigenvalues of $\hat{A}$ and so of $\tilde{A}$. Without loss we must therefore show that if $\tilde{\alpha}, \tilde{\gamma} > 0$, $\tilde{\beta}$ fixed, then the asymptotic phase of the eigenvalues of (14) is 0. But we know that, for any ϵ, there is C_ϵ (Simon 1970) with

$$|\tilde{\beta}|\, \|x^2\psi\| \leq \epsilon\|(\tilde{\alpha}p^2 + \tilde{\gamma}x^4)\psi\| + C_\epsilon\|\psi\|$$

and so since $\tilde{\alpha}p^2 + \tilde{\gamma}x^4$ has a real spectrum:

$$\|\, |\tilde{\beta}|x^2(\tilde{\alpha}p^2 + \tilde{\gamma}x^4 - E)^{-1}\psi\| \leq \epsilon(|E|/\mathrm{Im}\, E) + C_\epsilon(\mathrm{Im}\, E)^{-1}.$$

Since $\|A(A - E)^{-1}\| \leq |E|/\mathrm{Im}\, E$, and $\|(A - E)^{-1}\| \leq 1/\mathrm{Im}\, E$ for any self-adjoint A, and E cannot be an eigenvalue of (14) if $\|\, |\beta|x^2(\tilde{\alpha}p^2 + \tilde{\gamma}x^4 + -E)^{-1}\| < 1$, we have the required result on the asymptotic phase.

Step 7. We prove a general substantial result:

Theorem 2. Let P, Q be bounded operators on a Hilbert space with complete sets of generalised eigenvectors, so that the corresponding eigenvalues go to zero and are of finite multiplicity. Then any eigenvector of $P \otimes Q$ with eigenvalue $\lambda \neq 0$ is a *finite* sum of vectors of the form $\psi \otimes \omega$ with $P\psi = \mu\psi$, $Q\omega = \lambda\omega$.

Proof. Suppose that $(P-\mu)^k\psi=0$, $(Q-\lambda)^i\omega=0$. Then

$$(P\otimes Q-\mu\lambda)^{k+i}(\psi\otimes\omega)=\sum_{j=0}^{k+1}\binom{k+i}{j}[(P-\mu)^j\mu^{k+i-j}]\psi\otimes[Q^i(Q-\lambda)^{k+i-j}]\omega=0$$

Since $P\otimes Q-\mu\lambda=(P-\mu)\otimes Q+P\otimes(Q-\lambda)$ and since either $j\leq k$ or $k+i-j\geq i$. Thus by assumed completeness of the generalised eigenvectors of P, Q any Ψ is a limit of finite sums of generalised eigenvectors of $P\otimes Q$ each of the form $\psi\otimes\omega$.

Next we note that by general principles (Brown and Pearcy 1966), $\sigma(P\otimes Q)=\sigma(P)\sigma(Q)$ so by the hypothesis on $\sigma(P)$, $\sigma(Q)$, the spectrum of $P\otimes Q$ away from zero consists of isolated points.

Now let ψ be an eigenvector of $P\otimes Q$ with eigenvalue λ and let A be the generalised eigenprojection for λ (Reed and Simon 1978 p 316). If the space Ran A is not spanned by those $\psi\otimes\omega$ in Ran A, we can find $\tilde{\psi}$ orthogonal to all such $\psi\otimes\omega$ in Ran A. But we can find ψ_i, ω_i so that $\|\tilde{\Psi}-\bar{z}\psi_i\otimes\omega_i\|<\|A\|^{-1}\|\tilde{\Psi}\|$.

Noticing that $A(\psi_i\otimes\omega_i)$ is either 0 or $\psi_i\otimes\omega_i$ and that $\tilde{\Psi}$ is orthogonal to those $\psi\otimes\omega$ in Ran A, we see that $\tilde{\Psi}=0$. Thus $\Psi=\bar{z}\psi_i\otimes\omega_i$ with $\psi_i\otimes\omega_i$ in Ran A. By hypothesis there are only finitely many such possibilities. This is only possible if ψ_i, ω_i are eigenvectors rather than generalized eigenvectors. QED.

Step 8. The proof is complete except for one subtlety, namely: merely because $\exp(-a)\exp(-b)$ is an eigenvalues of $\exp(-c)$ we do not know that $a+b$ is an eigenvalue of C but only that $a+b+2n\pi i$ is an eigenvalue of C for some integer n. By using the trick on p 182 of Reed and Simon (1978) and Step 6 above this freedom of n is easily eliminated.

This completes the proof of Theorem 1.

Two of us (SG and VG) would like to thank the Department of Mathematics, Princeton University, for its hospitality. We would like to thank J Fröhlich for raising the question answered herein.

References

Balsev E and Combes J M *Commun. Math. Phys.* **22** 280

Benassi L, Grecchi V, Harrell E and Simon B 1978 *Phys. Rev. Lett.* to appear

Brown A and Pearcy C 1966 *Proc. Am. Math. Soc.* **17** 162

Epstein P S 1916 *Ann. Phys., (Lpz)* **50** 489

—— 1926 *Phys. Rev.* **28** 695

Graffi S and Grecchi V 1978 *Commun. Math. Phys.* **62** 83

—— 1979 *J. Phys. B: Atom. Molec. Phys.* **12** L265

Herbst I W 1979 *Commun. Math. Phys.* **64** 179

Herbst I W and Simon B 1978 *Phys. Rev. Lett.* **41** 67

Ichinose T 1970 *J. Reine Angew. Math.* **224** 119

—— 1972 *Trans. Ann. Math. Soc.* **170** 197

Jacobi C G J 1884 *Vorlesungen über Physik* (C Reiner)

Keldys M V 1951 *Dokl. Ak. Nauk SSR* **7** 11

Reed M and Simon B 1973 *J. Funct. Anal.* **13** 107

—— 1978 *Methods of Modern Mathematical Physics* vol 4 (New York: Academic)

Schechter M 1969 *J. Funct. Anal.* **4** 95

Schödinger E 1926 *Ann. Phys. (Lpz)* **80** 457

Simon B 1970 *Ann. Phys.* **58** 76

Titchmarsh E C 1958 *Eigenfunction Expansion* II (London: OUP)